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METHOD OF MANUFACTURING CERAMICS SINTERED BODY

(3-2-3)

[Abstract]

[Purpose]

It is the object of the present invention to provide a method of manufacturing a ceramics sintered body that is capable of efficiently manufacturing a sintered body having high strength, high thermal conductivity and excellent heat radiation properties as well as having few occurrences of deformations and color shading.

[Constitution]

A method of manufacturing a ceramics sintered body relating to the present invention comprises the steps of: forming a powder blend prepared by adding a sintered aid and amorphous carbon to an aluminum nitride powder in specified amounts to form a formed body of a specified shape, adjusting to a specified range the amount of carbon remaining in the formed body after degreasing, subjecting the formed body to deoxidation treatment by heating, and subsequently sintering the formed body in a non-oxidizing atmosphere. In addition, a powder blend may be subjected to deoxidation treatment prior to forming a formed body.

[Claims]

1. A method of manufacturing a ceramics sintered body comprising the steps of:

forming a powder blend prepared by adding a sintered aid and amorphous carbon to an aluminum nitride powder in specified amounts to form a formed body of a specified shape, adjusting to a specified range the amount of carbon remaining in the formed body after degreasing, subjecting the formed body to deoxidation treatment by heating, and subsequently sintering the formed body in a non-oxidizing atmosphere.

2. The method of manufacturing a ceramics sintered body according to claim 1, wherein the amount of amorphous carbon to be added is set at 0.1 to 1.5% by weight relative to the amount of the aluminum nitride powder.

3. The method of manufacturing a ceramics sintered body according to claim 1, wherein the amount of carbon remaining in the formed body after degreasing is set to be in the range of 0.15 to 0.5% by weight.

4. The method of manufacturing a ceramics sintered body according to claim 1, wherein the heating temperature during deoxidation treatment is set at 1,500°C to 1,650°C.

5. A method of manufacturing a ceramics sintered body comprising the steps of:

subjecting to deoxidation treatment by heating a powder

blend prepared by adding a sintering aid and 0.1 to 2% by weight of amorphous carbon to an aluminum nitride powder, pressure-forming the obtained powder blend subsequent to crushing to form a formed body, and subsequently sintering in a non-oxidizing atmosphere the obtained formed body after degreasing.

6. The method of manufacturing a ceramics sintered body according to claim 5, wherein the deoxidation treatment is performed in a non-oxidizing atmosphere heated to a temperature of 1,500 to 1,650°C.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a method of manufacturing a ceramics sintered body and more particularly to a method of manufacturing a ceramics sintered body having few occurrences of deformations and color shading as well as having high strength, high thermal conductivity and excellent heat radiation properties.

[0002]

[Prior Art]

Ceramics sintered bodies excellent in properties such as strength, heat resistance, corrosion resistance, abrasive

resistance, and lightweight properties as compared with the conventional metal materials have been widely utilized as machine parts, structural materials and decoration materials inclusive of semiconductors, electronic equipment materials, engine members, high-speed cutting tool materials, nozzles, and bearings, which are used under severe conditions for temperature, stress and abrasion the conventional metal materials cannot stand.

[0003]

In particular, an aluminum nitride (AlN) sintered body is an insulator of high thermal conductivity and has a thermal expansion coefficient close to that of silicon (Si), and thus is increasing its applications as a heat-dissipating substrate of highly integrated semiconductor devices.

[0004]

Conventionally, the above-mentioned ceramics sintered body is generally mass-produced by the manufacturing method below. That is, when aluminum nitride is used as a ceramic raw material, the manufacturing method involves first preparing a raw material blend by adding to an aluminum nitride powder a sintering aid, organic binders, and as required, a variety of additives, solvents, or dispersing agents, forming the obtained raw material blend by the doctor blade method into a thin-plate or sheet-like formed body, or press-forming the raw material blend to mold a thick-plate or large formed body, subjecting the obtained

formed body to degreasing treatment by heating in an air or nitrogen gas atmosphere, removing hydrocarbon components, etc. used as organic binders from the formed body, and subsequently heating the degreased formed body for densification to a high temperature in a nitrogen atmosphere, etc. to produce an aluminum nitride sintered body.

[0005]

In the above-mentioned manufacturing method, use of a hyperfine raw material powder with a mean particle diameter of about $0.3\text{ }\mu\text{m}$ or less as a raw material AlN powder, even if the AlN powder is singly used, results in the formation of a considerably densified sintered body. However, when large amounts of impurities such as oxygen deposited on the raw material powder surface, etc. are sintered, they become a solid solution in the AlN crystal lattice, or they generate complex oxides such as a Al-O-N compound, which prevents the transmission of lattice vibrations; as a result, the thermal conductivity of the AlN sintered body without use of a sintering aid is considerably low.

[0006]

On the other hand, when an AlN powder with a mean particle diameter of $0.5\text{ }\mu\text{m}$ or more is used as a raw material powder, the sintering properties are not good when the raw material is singly used, and so it is difficult for methods other than the hot press method to obtain a densified sintered body without

addition of an aid, leading to the disadvantage of low mass production. Hence, when a sintered body is efficiently produced by the normal-pressure sintering process, rare earth element oxides such as yttrium oxide (Y_2O_3), alkali earth metal oxides such as calcium oxide, etc. are generally added as sintering aids for densification of the sintered body and the prevention of the impurity oxygen in an AlN raw material powder becoming a solid solution in the AlN crystal particles.

[0007]

These sintering aids are thought to react with the impurity oxygen contained in an AlN raw material powder to form a liquid phase, thereby attaining densification of a sintered body, as well as fixing this impurity oxygen as a grain boundary phase to also achieve high thermal conductivity.

[0008]

[Problems to be solved by the Invention]

However, the conventional manufacturing methods make it extremely difficult to quantitatively control various impurities and causes the problems of producing large variations in sintering property (density) of each formed body and reducing the product yield due to increased amounts of deformations. In addition, remaining of impurities such as carbon produces in many cases deterioration of appearance qualities such as changing the color or producing the color shading, of a sintered body, and creates the disadvantage of further decreasing the yield

especially when the sintered body is used as a decoration material. In particular, oxygen contained as an impurity in a raw material powder or mixed in the manufacturing process is made replaced with nitrogen in the AlN crystal lattice during sintering to become a solid solution, which in turn lowers in many cases the high thermal conductivity of the largest available characteristic of AlN.

[0009]

The present invention has been made in order to solve the above-mentioned problems, and the object thereof is to provide a method of manufacturing a ceramics sintered body that is capable of efficiently manufacturing a sintered body having high strength, high thermal conductivity and excellent heat radiation properties as well as having few occurrences of deformations and color shading.

[0010]

[Means for solving the Problems]

The present inventors have conducted experiments and studies, in order to achieve the above-mentioned object, on the relations of the kinds of sintering aids to be added to raw material aluminum nitride powders and additives, the amounts of impurities remaining, compositions of sintered bodies, etc., and the effects thereof on the properties of the sintered bodies by changing them in various ways, and have found the findings below.

[0011]

In other words, the present inventors found that the amount of carbon remaining in the formed body prior to sintering and thus the degreased body greatly affects the quality of the finally produced sintered body. FIG. 1 is a graph that illustrates plots of the thermal conductivity, sintering properties, amount of deformation, and the degree of color shading versus the amount of carbon remaining in the degreased body for sintered bodies.

[0012]

As shown in FIG. 1, when the amount of carbon remaining in the degreased body is reduced as much as possible, the sintering properties of the formed body and thus the density, amount of deformation and color shading of the formed body become constant. On the other hand, it has been found that a proper amount of carbon remaining is required in order to keep the thermal conductivity high. A small amount of carbon remaining reduces the oxygen deposited on the raw material powder surface and oxygen present in oxides to generate CO and CO₂, which are discharged to the outside of the system. Carbon remaining in an excessive amount, however, produces, like other impurities, carbides preventing thermal conductance, or prevents the formation of a liquid phase necessary during sintering to decrease sintering properties, thereby producing a sintered body having low densification and low strength.

[0013]

Therefore, it is found that adjustment of the amount of

carbon remaining in the degreased body in an appropriate range, as discussed above, enables the production of a sintered body having few occurrences of deformations and color shading as well as having a high density and high thermal conductivity. However, the prior art conventional manufacturing method makes it extremely difficult to set the amount of carbon remaining to be in a suitable range. For example, when a raw material blend to which an organic binder is added is formed to mold a sheet formed body, which is then degreased in air at a temperature of about 400°C, the amount of carbon remaining in the degreased body becomes as extremely small as about 0.01% by weight, while for a large formed body, the impurities are difficult to remove and thus conversely the amount of carbon remaining is significantly increased, at any rate, leading to difficult setting to an optimal range.

[0014]

Under the circumstances, previous addition of a material to be a carbon source to a raw material AlN powder in a specified amount keeps the amount of carbon remaining in a specified range, the remaining carbon reducing and removing impurities such as oxygen during sintering, which has been proved to be effective in improving properties of the sintered body.

[0015]

In other words, it has been found that setting to a specified range the amount of carbon remaining in a formed body prior to

sintering and thus subsequent to degreasing by adding to the raw material AlN powder a specified amount of amorphous carbon as an additive, enables substantial reduction of the amounts of impurities in a sintered body as well as obtainment of a sintered body having high strength and few occurrences of deformations and color shading.

[0016]

In addition, it has been shown that heating to an elevated temperature a raw material blend having amorphous carbon and a sintering aid effectively removes oxygen contained in the raw material blend and that use of this deoxidized raw material blend permits the production of a high quality sintered body with few disadvantages mentioned above, even though a sintered body is large.

[0017]

The present invention has been established on the basis of the above-mentioned findings. Namely, a method of manufacturing a ceramics sintered body relating to the present invention comprises the steps of: forming a powder blend prepared by adding a sintered aid and amorphous carbon to an aluminum nitride powder in specified amounts to form a formed body of a specified shape, adjusting to a specified range the amount of carbon remaining in the formed body after degreasing, subjecting the formed body to deoxidation treatment by heating, and subsequently sintering the formed body in a non-oxidizing

atmosphere.

[0018]

In addition, suitably, the amount of amorphous carbon to be added is set at 0.1 to 1.5% by weight relative to the amount of the aluminum nitride powder.

[0019]

Furthermore, suitably, the amount of carbon remaining in a sintered body subsequent to degreasing is set to be in the range of 0.15 to 0.5% by weight.

[0020]

Also, suitably, the heating temperature during deoxidation treatment is set at 1,500°C to 1,650°C.

[0021]

Also, a method of manufacturing another ceramics sintered body relating to the present invention comprises the steps of: subjecting a powder blend prepared by adding a sintering aid and 0.1 to 2% by weight of amorphous carbon to an aluminum nitride powder to deoxidation treatment by heating; pressure-forming the obtained powder blend subsequent to crushing to form a formed body; and subsequently sintering in a non-oxidizing atmosphere the obtained formed body after degreasing.

[0022]

Additionally, suitably, the deoxidation treatment is performed in a non-oxidizing atmosphere heated to a temperature of 1,500 to 1,650°C.

[0023]

For an aluminum nitride (AlN) powder for use in the present invention and being the primary component of a sintered body, the content of oxygen is controlled to be 2% by weight or less taking into account the sintering properties and thermal conductivity, with the mean particle diameter being 0.05 to 5 μm , preferably 3 μm or less.

[0024]

As sintering aids, oxides and nitrides of the rare earth elements (e.g., Y, Sc, Ce, Dy, etc.), the oxides of the alkali earth metal (Ca), or materials that are subjected to sintering operation to yield these compounds are used, and particularly yttrium oxide (Y_2O_3) and calcium oxide (CaO) are preferably used. The amount of sintering aid to be added is adjusted in the range of 0.5 to 7.5% by weight. When the amount of addition is less than 0.5% by weight, the sintering properties are not sufficiently improved, thus leading to the formation of a sintered body with low strength and no densification, or resulting in oxygen becoming a solid solution in the AlN crystal. As a result, a sintered body having high thermal conductivity cannot be formed. On the other hand, when the amount of addition is excessive, and thus exceeds 7.5% by weight, grain boundary phases remain in the sintered body, or the volume of grain boundary phases removed by heat treatment becomes large, and so voids may remain in the sintered body to increase the degree of shrinkage

and readily cause deformations.

[0025]

Amorphous carbon acts as reducing impurities such as oxygen during sintering to remove them to the outside of the system, and thus it is added to a raw material AlN powder in the range of 0.1 to 1.5% by weight. When the amount of addition is as too small as less than 0.1% by weight, the effect of deoxidation by amorphous carbon during sintering becomes insufficient to be unable to obtain a sintered body of high thermal conductivity. On the other hand, addition of an excessive amount of more than 1.5% by weight readily causes deformations and color shading of a sintered body, thus resulting in the deterioration of sintering properties and thermal conductivity. More preferably, the amount of carbon remaining in a sintered body subsequent to degreasing is set to be in the range of 0.15 to 0.5% by weight, which permits a high quality sintered body having properties of deformation, color shading, sintering properties and thermal conductivity balanced.

[0026]

Amorphous carbon does not burn in a normal degreasing treatment temperature range (375 to 450°C) and remains in the formed body. As the temperature exceeds 450°C, it starts burning little by little. Therefore, amorphous carbon is highly effective as a carbon source that controls the amount of carbon remaining in a formed body after degreasing treatment.

[0027]

In addition, graphite, a typical example of amorphous carbon, does not decompose or evaporate even though it is treated at a high sintering temperature and remains in the sintered body to produce impurity oxides, etc., and so it is not preferable.

[0028]

Moreover, the above-mentioned amorphous carbon is a carbon powder with a mean particle diameter of 0.5 μm or less in order to enhance dispersibility in a raw material powder blend, and also to prevent the degradation of heat transfer properties of a sintered body caused by ash produced by heat treatment in air, it is recommendable to use an amorphous carbon powder with an ash content of 1% by weight or less. The examples include Carbon Black R-30 (available from Mitsubishi Chemical Media Co., Ltd.).

[0029]

Applicable forming methods include the sheet forming methods such as the general-purpose mold press method, the hydrostatic press method and the doctor blade method.

[0030]

Following the above-mentioned forming operation, a formed body was heated to a temperature of 375 to 450°C in an oxidizing atmosphere, for example in air, to remove an organic binder added in advance. Even in degreasing treatment, the amorphous carbon previously added in a specified amount remains in the degreased formed body as it is.

[0031]

Subsequently, the degreased formed body is subjected to deoxidation treatment prior to sintering. Deoxidation treatment is that which heats the degreased formed body to a specified temperature to remove the impurity oxygen contained in the formed body via reduction action of the above-mentioned amorphous carbon and which is carried out by heating the formed body to 1,500 to 1,650°C in a non-oxidizing atmosphere. When the temperature is less than 1,500°C, the body becomes a composition having remaining oxygen in quantity due to insufficiency in the above-mentioned deoxidation action. On the other hand, when the heating temperature exceeds 1650°C, sintering densification partially starts and thus the discharge of gases (CO, CO₂) bonded to oxygen becomes difficult; as a result, the remaining oxygen ratio increases at any rate.

[0032]

Then, the formed body subjected to deoxidation treatment is sintered. Sintering operation is carried out by heating the formed body at a temperature of 1,700 to 2,000°C for about 2 to 5 hours in a non-oxidizing atmosphere such as in nitrogen gas. The sintering is performed in a nitrogen gas or in a reducing atmosphere containing nitrogen gas. H₂ gas or CO gas may be used as a reducing gas. Moreover, the sintering may be conducted in an atmosphere such as in a vacuum (including a slightly reducing atmosphere), under a reduced pressure, in a pressurized

atmosphere or in a normal atmospheric pressure. Firing at a low temperature, i.e., at a sintering temperature of less than 1,700°C, hardly obtains a densified sintered body although the results depend on the particle diameter of a raw material powder or the content of oxygen. On the other hand, firing at a temperature higher than 2000°C has the possibility of the vapor pressure of AlN itself becoming high leading to difficulty in densification. As a result, the sintering temperature is set to the above-mentioned range.

[0033]

Now, another manufacturing method concerning the present invention indicated in claim 5 will be described.

[0034]

In the above-mentioned manufacturing method according to claim 1, deoxidation treatment is performed in the stage when the material is a formed body, while the manufacturing method according to claim 5 possesses a marked feature of subjecting a powder blend to which a specified amount of amorphous carbon is added in advance to deoxidation treatment in the stage when the material is in powder form.

[0035]

In the manufacturing method, the deoxidation treatment conditions, deoxidation atmosphere, degreasing treatment conditions, sintering conditions, sintering atmosphere, etc. are the same as the corresponding conditions in the manufacturing

method according to claim 1. However, in the deoxidation treatment in a powder state, the upper limit to the amount of amorphous carbon to be added is set at 2% by weight due to much outflow of carbon vapor. In addition, deoxidation in a powder state partially solidifies a raw material powder blend to drop the flowability, which in turn lowers die-feedability leading to difficulty in even feed, and so the crushing step is set prior to forming operation.

[0036]

According to the manufacturing method, a raw material powder blend undergoes deoxidation treatment in a powder state and the oxygen concentration thereof is sufficiently reduced. Thus, while deoxidation treatment in the form of a formed body makes it difficult to discharge gases (CO, CO₂) bonded to oxygen from the formed body, the method of the present invention is excellent in efficiency of removing oxygen. Accordingly, for the production of a large, thick sintered body, the manufacturing method according to claim 5, which readily discharges gas, is appropriate.

[0037]

A aluminum nitride sintered body produced by the above-mentioned manufacturing method, as a polycrystal, has a very high thermal conductivity of 200 w/m k or more and high strength as well as exhibiting little deformation or color shading.

[0038]

[Operation]

The method of manufacturing a ceramics sintered body relating to the above-mentioned constitution involves adding a specified amount of amorphous carbon to an aluminum nitride powder to form a raw material power blend, and then subjecting to deoxidation treatment this raw material power blend in a powder state or in the form of a formed body, leading to the removal of the impurity oxygen contained in the raw material blend or in the formed body through the reduction action of the above-mentioned amorphous carbon.

[0039]

As a result, an aluminum nitride sintered body produced by the above-mentioned manufacturing method has little effect of impurities and oxides, shows high thermal conductivity and high strength, as well as exhibiting little deformation or color shading.

[0040]

[Examples]

The effects of the method of manufacturing a ceramics sintered body relating to the present invention will hereinafter be described in more detail by means of examples.

[0041]

Examples 1 to 6

To an aluminum nitride containing 1.0% by weight of oxygen

as an impurity and having a mean particle diameter of $1.5\text{ }\mu\text{m}$ was added 5% by weight of Y_2O_3 (yttrium oxide) as a sintering aid and further to this was added amorphous carbon with a mean particle diameter of $0.3\text{ }\mu\text{m}$ (Carbon Black: R30, ash content: 0.01% by weight or less) in a range of 0.1 to 1.5% by weight as indicated in Table 1, and the resulting material was subjected to wet mixing in ethanol for 30 hours followed by drying to thereby prepare powder blends for Examples 1 to 6. Thereafter, each powder blend obtained by drying was fed into the molding die of a press molding machine and was compression molded at an application pressure of $1,200\text{ kg/cm}^2$ to prepare many formed bodies of disk-like heat radiating plates and subsequently each formed body was degreased by heating in air at a temperature of 375°C for two hours. The amount of carbon contained in each formed body (degreased body) subsequent to degreasing treatment was almost the same as the amount of amorphous carbon initially added to the raw material AlN powder.

[0042]

Then, each formed body subjected to degreasing treatment was placed in a heating furnace filled with N_2 gas and subjected to deoxidation treatment by heating for one hour in a temperature range of $1,500$ to $1,650^\circ\text{C}$. Thereafter, each formed body subjected to deoxidation treatment was heated to a temperature of $1,815^\circ\text{C}$ and maintained for 4 hours for densification sintering to thereby prepare AlN ceramics sintered bodies with a diameter

of 60 mm and a thickness of 2.0 mm for Examples 1 to 6.

[0043]

Comparative Example 1

On the other hand, an AlN ceramics sintered body having the same dimensions as in Example 1, relating to Comparative Example 1, was prepared under the same conditions as in Example 1 except that amorphous carbon was not added and that deoxidation treatment was not performed.

[0044]

Comparative Example 2

In addition, an AlN ceramics sintered body having the same dimensions as in Example 5, relating to Comparative Example 2, was prepared under the same conditions as in Example 5 except that amorphous carbon was added in an amount of as excessive as 2.0% by weight.

[0045]

Comparative Example 3

Furthermore, an AlN ceramics sintered body having the same dimensions as in Example 3, relating to Comparative Example 3, was prepared under the same conditions as in Example 3 except that the preparation was made to directly proceed to the sintering treatment subsequent to degreasing without undergoing the deoxidation treatment step for the degreased body.

[0046]

Then, each of the obtained AlN ceramics sintered bodies

relating to Examples 1 to 6 and Comparative Examples 1 to 3 was determined for the degree of the deformation, the presence or absence of color shading, sintering density, and thermal conductivity in order to evaluate the properties thereof. The results are given in the right-hand section of Table 1 below.

[0047]

[Table 1]

| Sample No. | Amount of amorphous carbon to be added (% by weight) | Deoxidation treatment conditions for degreased body (temperature x time) | Properties of sintered body | | | |
|-----------------------|--|--|-----------------------------|---------------|------------------------------|------------------------------|
| | | | Amount of deformation | Color shading | Density (g/cm ³) | Thermal conductivity (W/m·K) |
| Example 1 | 0.1 | 1500°C x 1hr | Small | Absent | 3.31 | 202 |
| Example 2 | 0.2 | 1600°C x 1hr | Small | Absent | 3.31 | 209 |
| Example 3 | 0.4 | 1550°C x 1hr | Small | Absent | 3.30 | 225 |
| Example 4 | 0.8 | 1550°C x 1hr | Small | Absent | 3.29 | 214 |
| Example 5 | 1.0 | 1600°C x 1hr | Intermediate | Absent | 3.29 | 209 |
| Example 6 | 1.5 | 1650°C x 1hr | Intermediate | Absent | 3.28 | 201 |
| Comparative Example 1 | 0 | None | Small | Absent | 3.31 | 170 |
| Comparative Example 2 | 2.0 | 1600°C x 1hr | Large | Present | 3.10 | 155 |
| Comparative Example 3 | 0.4 | None | Large | Present | 3.18 | 183 |

[0048]

The results in Table 1 show that the ceramics sintered bodies relating to Examples 1 to 6, wherein an appropriate amount of amorphous carbon was added and deoxidation treatment was performed that effectively removes the impurity oxygen in the degreased body by utilizing reduction action during heating of the amorphous carbon, have few occurrences of deformations and color shading as well as having high density (high strength), high thermal conductivity and excellent heat radiation properties as compared with Comparative Examples 1 and 2.

[0049]

On the other hand, the sintered body as in Comparative Example 1, wherein amorphous carbon was not added and deoxidation treatment was not performed, has few occurrences of deformations and color shading, but has an oxide phase generated in the crystal grain boundary thereof by the impurity oxygen resulting in a drop in thermal conductivity.

[0050]

In addition, when an excessive amount of amorphous carbon was added as in Comparative Example 2, excess carbon is likely to remain in the sintered body, which significantly causes deformation and color shading as well as deteriorating sintering properties and dropping strength and thermal conductivity.

[0051]

Furthermore, as shown in Comparative Example 3, although

the amount of amorphous carbon added is within an appropriate range, the degreased body surface is partially densified when the preparation is made to directly proceed to the sintering treatment without undergoing the deoxidation treatment, and so carbon bonded to the impurity oxygen resists being discharged to the outside of the degreased body and thus remains. For this reason, the sintered body has large degrees of deformation and color shading as well as having a low density and a dropped thermal conductivity.

[0052]

There is hereinafter discussed examples wherein a raw material powder prior to molding operation is subjected to deoxidation treatment in advance, and then a large, thick plate-like sintered body is produced.

[0053]

Examples 7 to 11

To an aluminum nitride containing 1.0% by weight of oxygen as an impurity and having a mean particle diameter of 1.5 μm was added 5% by weight of Y_2O_3 (yttrium oxide) as a sintering aid and further to this was added amorphous carbon with a mean particle diameter of 0.3 μm (Carbon Black: R30, ash content: 0.01% by weight or less) in a range of 0.1 to 2.0% by weight as indicated in Table 2, and the resulting material was subjected to wet mixing in ethanol for 30 hours followed by drying to thereby prepare powder blends for Examples 7 to 11. Then, each formed

body subjected to degreasing treatment was placed in a heating furnace filled with N_2 gas and subjected to deoxidation treatment by heating for one hour in a temperature range of 1,500 to 1,650°C as indicated in Table 2. The powder blend subjected to deoxidation treatment was partly coagulated to become masses, and this mass-like powder blend was crushed via a ball mill in a nitrogen gas atmosphere to give a ground powder blend.

[0054]

Subsequently, to each crushed powder blend was added an organic binder and evenly mixed and then each mixed powder blend was fed into a molding die. The blend was compression molded at an application pressure of 1,200 kg/cm² to prepare many formed bodies of disk-like heat radiating plates and subsequently each formed body was degreased by heating in air at a temperature of 375°C for two hours.

[0055]

Then, each formed body subjected to degreasing treatment was placed in a heating furnace filled with N_2 gas and the inside of the furnace was heated to a temperature of 1,815°C and maintained for 4 hours for densification sintering to thereby prepare thick, large AlN ceramics sintered bodies with a diameter of 120 mm and a thickness of 25 mm relating to Examples 7 to 11.

[0056]

Comparative Example 4

On the other hand, an AlN ceramics sintered body having the same dimensions as in Example 7, relating to Comparative Example 4, was prepared under the same conditions as in Example 7 except that amorphous carbon was not added and that deoxidation treatment was not performed.

[0057]

Comparative Example 5

In addition, an AlN ceramics sintered body having the same dimensions as in Example 8, relating to Comparative Example 5, was prepared under the same conditions as in Example 8 except that amorphous carbon was added in an amount of as excessive as 3.0% by weight.

[0058]

Comparative Example 6

Furthermore, a ceramics sintered body having the same dimensions as in Example 9, relating to Comparative Example 6, was prepared under the same conditions as in Example 9 except that the preparation was made to directly proceed to the sintering treatment subsequent to molding and degreasing without undergoing the deoxidation treatment step for the degreased body.

[0059]

Then, each of the obtained AlN ceramics sintered bodies relating to Examples 7 to 11 and Comparative Examples 4 to 6 was determined for the degree of the deformation, the presence or absence of color shading, sintering density, and thermal

conductivity in order to evaluate the properties thereof. The results are given in the right-hand section of Table 2 below.

[0060]

[Table 2]

| Sample No. | Amount of amorphous carbon to be added (% by weight) | Deoxidation treatment conditions for degreased body (temperature x time) | Properties of sintered body | | | |
|-----------------------|--|--|-----------------------------|---------------|------------------------------|------------------------------|
| | | | Amount of deformation | Color shading | Density (g/cm ³) | Thermal conductivity (W/m·K) |
| Example 7 | 0.1 | 1500°C x 1hr | Small | Absent | 3.31 | 203 |
| Example 8 | 0.3 | 1600°C x 1hr | Small | Absent | 3.31 | 219 |
| Example 9 | 0.5 | 1600°C x 1hr | Small | Absent | 3.30 | 222 |
| Example 10 | 1.0 | 1650°C x 1hr | Small | Absent | 3.29 | 228 |
| Example 11 | 2.0 | 1600°C x 1hr | Small | Absent | 3.26 | 210 |
| Comparative Example 4 | 0 | None | Small | Absent | 3.31 | 170 |
| Comparative Example 5 | 3.0 | 1600°C x 1hr | Intermediate | Present | 3.12 | 156 |
| Comparative Example 6 | 0.5 | None | Large | Present | 3.16 | 178 |

[0061]

The results in Table 2 show that the ceramics sintered bodies relating to Examples 7 to 11, wherein an appropriate amount of amorphous carbon was added and deoxidation treatment was performed that effectively removes the impurity oxygen in the degreased body in advance by utilizing reduction action during heating of the amorphous carbon, have few occurrences of deformations and color shading as well as having high density (high strength), high thermal conductivity and excellent heat radiation properties as compared with Comparative Examples 4 and 5.

[0062]

In particular, in Examples 7 to 11, a raw material powder blend is previously subjected to deoxidation treatment in powder form, and so the discharge of carbon bonded to the impurity oxygen is extremely easy as compared with the case where deoxidation treatment is performed in the form of a formed body. Hence, the method of these examples is effective when a thick plate-like or large sintered body is produced.

[0063]

On the other hand, the sintered body as in Comparative Example 4, wherein amorphous carbon was not added and the deoxidation treatment of a raw material powder blend was not performed, has few occurrences of deformations and color shading, but has an oxide phase generated in the crystal grain boundary

thereof by the impurity oxygen leading to a drop in thermal conductivity.

[0064]

In addition, when an excessive amount of amorphous carbon was added as in Comparative Example 5, excess carbon is likely to remain in the sintered body, which significantly causes deformation and color shading as well as deteriorating sintering properties and dropping strength and thermal conductivity.

[0065]

Furthermore, as shown in Comparative Example 6, although the amount of amorphous carbon added is within an appropriate range, the degreased body surface is partially densified when the preparation is made to directly proceed to the sintering treatment subsequent to molding and degreasing without undergoing the deoxidation treatment, and so carbon bonded to the impurity oxygen resists being discharged to the outside of the degreased body and thus remains. For this reason, the sintered body has large degrees of deformation and color shading as well as having a low density and a dropped thermal conductivity.

[0066]

[Advantages of the Invention]

As discussed thus far, a method of manufacturing a ceramics sintered body relating to the present invention comprises the steps of: adding a specified amount of amorphous carbon to an aluminum nitride powder to form a raw material power blend; and

then subjecting this raw material power blend in a powder state or in the form of a formed body to deoxidation treatment, leading to the removal of the impurity oxygen contained in the raw material blend or in the formed body through the reduction action of the above-mentioned amorphous carbon.

[0067]

As a result, an aluminum nitride sintered body produced by the above-mentioned manufacturing method has little effect of impurities and oxides, shows high thermal conductivity and high strength, as well as exhibiting little deformation or color shading.

[Brief Description of the Drawing]

FIG. 1 is a graph that illustrates plots of the thermal conductivity, sintering properties, amount of deformation, and the degree of color shading versus the amount of carbon remaining in the degreased body for sintered bodies.

Fig. 1

